Modeling the high pressure behavior of the actinide monopnictides and monochalcogenides

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Abstract

At ambient temperature and pressure, a majority of the actinide monopnictides and monochalcogenides exhibit a face-centered cubic (f.c.c.) structure (NaCl-type, B1). Two exceptions are ThTe and ThBi, which have a body-centered cubic (b.c.c.) structure (CsCl-type, B2). Several of these B1 compounds undergo at least one structural transformation under pressure. Frequently, the transition is from the initial NaCl-type to a CsCl-type cubic structure, although other structural forms are encountered. In addition to providing structural information, high pressure studies reveal important information about chemical bonding. Presented here are efforts to generate a pseudo-ionic model and geometrical correlations for these materials, which are useful for predicting the high pressure transition pressures, structures and volume changes accompanying the transitions. This model relies on ionic radii and lattice parameters at ambient pressure as the input parameters. One of the correlations established is that plots of transition pressures as a function of the ratio of the radii ($r_{An^{y+}}/r_{X^{z-}}$; $An \equiv$ actinide, $X \equiv$ metalloid), for a specific pnictide or chalcogenide anion, can be fitted by a first-order equation: $P(\text{GPa}) = -339 r^+/r^- + C$, where $C = 174$, 145 or 136, respectively, for anions of the fourth, fifth or sixth periods in the Periodic Table. Correlations were also found for volume collapses accompanying the phase transitions, but these were more complex in nature.

1. Introduction

The actinide monopnictides and monochalcogenides (AnX) have been systematically studied under high pressure, and the experimental results obtained allow us to find both qualitative and quantitative explanations for their observed phase transitions. The prediction of the transition pressures requires an understanding of the effects of pressure on the chemical bonding.

However, in the case of the actinide monopnictides and monochalcogenides (AnX), there has not been a theoretical model which successfully predicts the transition pressures, the volume collapses and the bulk moduli. The AnX compounds, many of which have already been studied by high pressure X-ray diffraction [1–9], provide systematic trends in series of compounds and may provide an empirical key to understanding pressure effects.

We have compiled here data, collected at ambient and high pressures, for the crystal structures, the lattice parameters, the ionic radii, the volume collapses and the bulk moduli of AnX compounds. The principal

goals of this study were (1) to examine the systematic relationship between the transition pressures, the volume collapses and the bulk moduli and the size of ions; and (2) to provide a model (geometrical correlation) based on ionic bonding for predicting high pressure behavior using the lattice parameters at normal pressure.

2. Geometrical model

At ambient pressure, the actinide monopnictides and monochalcogenides exhibit a face-centered cubic (f.c.c.) structure (NaCl-type, B1), except for ThTe and ThBi, which have a body-centered cubic (b.c.c.) structure (CsCl-type, B2). Under high pressures, most undergo a crystallographic phase transition from the B1 to the B2 structure.

2.1. The transition pressure and hypotheses for the ionic bonding

To initiate this work, we assumed ionic bonding and used a developed relationship based on radii ratios (such as the ratio of the cation radius to the anion radius, *i.e.* $r_{An^{y+}}/r_{X^{z-}}$).

Ionic bonding occurs as a result of electrostatic interaction between ions of opposed charges, which

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generally have a distribution of charges of spherical symmetry. We have considered here a hard sphere model and we have assumed that one ion is touching its nearest neighbors (such as the case of NaCl). In developing this hypothesis, we found that the best relationships were obtained when a 4+ charge was assigned to the actinides and a 3− or 2− charge to the anions. Although this is at first disturbing, it does provide a working situation. For example, the lattice parameters calculated with these radii are in good agreement with those measured experimentally by X-ray diffraction. A rational explanation why the charges selected above work is that the bonds are not fully ionic (the "extra" electrons may be involved in metallic bondings). These "unexpected charges" compensate for the covalent character of the bond. The 4+ cation radius is taken from Shannon [10].

The cation, roughly 2.5 times smaller than the anion, is the most difficult to deform. Consequently, in all the molecules considered in the following figures, the radius of a given cation can be taken to be the same for a given coordination number (CN). For a hard sphere model, the radius of the anion is then calculated from the measured lattice parameter as follows:

$$r_{X^-} = \frac{a_0}{2} - r_{An^{4+}}$$

where r_{X^-} is the radius of the anion, $r_{An^{4+}}$ is the radius of the cation and a_0 is the lattice parameter.

The results of this empirical approach appear in Figs. 1 and 2, where we have plotted the transition pressures as a function of the ratio $r_{An^{4+}}/r_{X^{2-}}$. Figure 1 describes the variation of the transition pressures in the actinide monopnictides, while Fig. 2 summarizes the same variation for the chalcogenide analogs. The points corresponding to the arsenides, antimonides, bismuthides, selenides and tellurides of the actinides studied fall on a straight line. The examples for the families of straight lines obtained are as follows: for AnAs, $p = -342$,
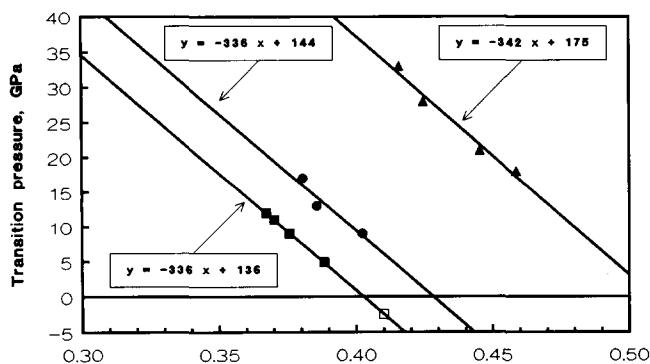

Fig. 1. Variation of the transition pressure p as a function of the ratio of the ionic radii $r_{An^{4+}}/r_{X^{2-}}$ in the actinide monopnictides: ▲, AnAs; ●, AnSb; ■, AnBi; □, ThBi.
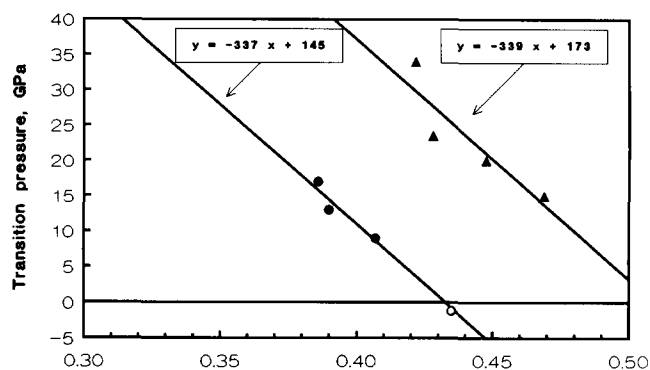

Fig. 2. Variation of the transition pressure p as a function of the ratio of the ionic radii $r_{An^{4+}}/r_{X^{2-}}$ in the actinide monochalcogenides: ▲, AnSe; ●, AnTe; ○, ThTe.

$r + 175$; for AnSb, $p = -336, r + 144$; for AnBi, $p = -336$, $r + 136$; for AnSe, $p = -339, r + 173$; for AnTe, $p = -337$, $r + 145$. Here, p is the observed transition pressure and r is the ratio of the ionic radius of the anion to that of the cation (CN = 6).

We have not attempted to give a physical explanation of the slopes or the intercepts. However, there are some features to note:

(1) All the points fall on parallel straight lines.

(2) The line associated with a series of compounds (such as the actinide arsenides) has a slope and intercept with similar values to those of a series of anions in the same period (such as the actinide selenides). Lines of common slope and intercept would occur with compounds of Sb + Te, Bi + Po, etc.

(3) An interesting situation is found for ThTe and ThBi when their data are plotted in Figs. 1 and 2. These two compounds constitute exceptions, since, at ambient pressure, they have the structure that their analogs possess at high pressure (B2). Thus, from our model, these two compounds appear to have undergone a phase transition at a negative pressure. If we calculate for ThTe and ThBi the ratio of the ionic radii for a structure of the NaCl-type, one obtains extrapolated values for their transition pressures at −1.5 and −2.5 GPa respectively. ThBi has the B2 structure at ambient pressure and, using this plot, it is interesting to speculate that ThPo could have the same structure and indicate a smaller negative transition pressure.

From the calculations carried out, we have deduced a linear regression system which, when associated with the ionic model hypothesis, estimates the phase transition pressures, assuming the lattice parameter of the compound at ambient temperature and pressure is known. The general equation is as follows:

$$p = -339r + C$$

where $C = 174$ for an anion of the fourth period, $C = 145$ for an anion of the fifth period and $C = 136$ for an anion of the sixth period.

2.2. The volume collapse

We analyzed the variation of the volume collapse for the first-phase transition as a function of the ion radius ratios. This relationship is presented similarly to the transition pressure developed above, and Figs. 3 and 4 display our results. Here again, the points may be fit to straight lines. A linear regression calculation then leads to the following: for AnAs, $V = -23, r + 21$; for AnSb, $V = -70, r + 39$; for AnBi, $V = -225, r + 98$; for AnSe, $V = -44, r + 29$; for AnTe, $V = -16, r + 14$. Here, V is the observed volume collapse at the B1–B2 phase transition, and r is the ratio $r_{An^{4+}}/r_{X^{2-}}$ (CN = 6).

We have noticed that an increase in the radius ratio leads to a decrease in magnitude of the volume collapse observed at the first-order phase transition. In the actinide monopnictides, the larger the anion is, the more negative is the slope. The opposite is true for the monochalcogenide analogs. In contrast to what was said above for the evolution of the transition pressure,
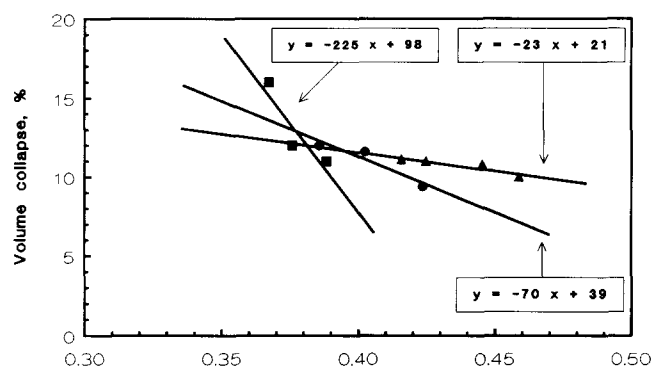
it is more difficult to make comparisons between the arsenides and the selenides and between the antimonides and the tellurides.

2.3. The bulk modulus

The next effort will be the development of a model capable of predicting B_0.

3. Conclusions

The study of the data which have been compiled from X-ray diffraction measurements under high pressure in actinide monopnictides and monochalcogenides has allowed us to develop a model which considers ionic bonding. This model explains the observed phenomena (transition pressure and volume collapse), and permits the prediction of the behavior (transition pressure and volume collapse) for actinide compounds under pressure. This prediction only requires the lattice parameter of the compound at ambient pressure and temperature.

Fig. 3. Variation of the volume collapse V as a function of the ratio of the ionic radii $r_{An^{y+}}/r_{X^{z-}}$ in the actinide monopnictides: ▲, AnAs; ●, AnSb; ■, AnBi.
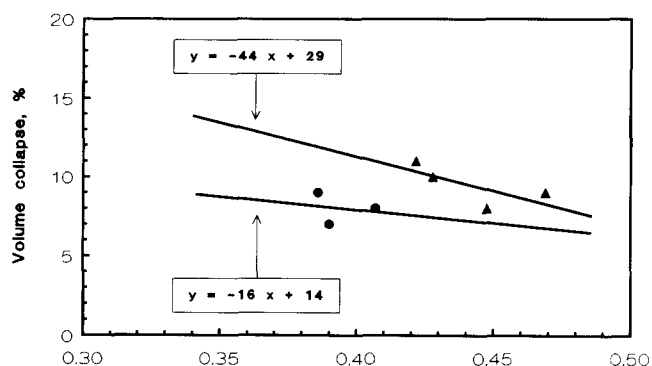

Fig. 4. Variation of the volume collapse V as a function of the ratio of the ionic radii $r_{An^{y+}}/r_{X^{z-}}$ in the actinide monochalcogenides: ▲, AnSe; ●, AnTe.

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